

# PATENT SPECIFICATION

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## (54) LUBRICANT COMPOSITIONS

(71) We, THE LUBRIZOL CORPORATION, a corporation duly organised and existing under the laws of the State of Ohio, United States of America, of Box 17100 Euclid Station, Cleveland, Ohio 44117, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns lubricating oil compositions which are especially adapted for use in mechanical systems where gears are subjected to great stresses and extremely high pressures such as those found in automotive rear axle and tractor transmissions.

The problems associated with the lubrication of automotive rear axle and transmission gears are well known to those of skill in the art. Such gears are usually hypoid and for reasons inherent in their design develop great pressures between the contacting metal surfaces of the gear. These pressures literally squeeze out ordinary mineral oil lubricants from between the gears and results in metal-to-metal contact between the parts of the gear under extreme high pressures. Such metal-to-metal contact soon leads to deformation and destruction of the gear surfaces.

To alleviate these and other problems it has become a common practice to add to gear oils certain chemical substances which are generally called additives. Among such additives are extreme pressure agents which are widely believed to react with the metal surfaces of the gear under the elevated temperatures and high pressures generally encountered during operation of the gear to form thin films. These newly formed layers act as separants and lubricants for the gear surfaces and thus prevent

or reduce destructive metal-to-metal contact.

Recently a demand has arisen for lubricants which will function satisfactorily as gear lubricants under a wide range of temperature conditions. Such compositions are characterized by a relatively small change in their viscosity with changing temperature and they are commonly graded according to SAE standards so as to meet the requirements of a winter grade and a normal grade. Such oils are said to be "multigraded." Such multigraded gear lubricants can also be said to have high viscosity indices. Multigraded gear lubricants thus have the desirable property of being able to function immediately, though cold, upon being put into service and continue to function satisfactorily as they become heated during operation.

In addition to being multigraded, it is desirable that lubricant compositions especially adapted for use as gear lubricants exhibit shear stability. This means that they will not degrade or lose their viscosity as a result of the shearing forces encountered during their use. Compositions exhibiting desirable shear stability will be found to generally have a viscosity within 85 to 95% of their original viscosity after many hours (say 1000) of service. It has been recognized that many ordinary viscosity index improvers commonly added to crankcase lubricating oils, such as high molecular weight (greater than 10,000) polyisobutylene and polyacrylates, do not possess the desired shear stability for use in improving the viscosity properties of gear lubricants, even though used with extreme pressure additives.

It has now been found that multigrade lubricants exhibiting good shear stabilities can be made by combining in certain proportions

base oils, polymers of specified structure and molecular weight and extreme pressure agents.

According to the invention, there is provided a lubricating oil composition comprising  
 5 (A) at least 30, preferably 90 to 50, weight percent of a base oil having a viscosity of 40 to 2000 SUS at 100° F, (B) at least one extreme pressure agent in an amount sufficient to improve its extreme pressure properties, and  
 10 (C) at least 5 weight percent of at least one oil-soluble homopolymer (as hereinafter defined) of a non-aromatic mono-olefin having at least 3 carbon atoms, said polymer having a number average molecular weight of 750 to  
 15 10,000 and being present in an amount such as to allow the lubricating oil composition to be a multigraded gear oil having a minimum winter grade of SAE 75W and a maximum normal grade of SAE 250, with the proviso that when the base oil is a mixture of synthetic  
 20 and natural oils (as hereinafter defined), it contains 5 to 95 weight percent of at least one synthetic oil.

The base oils of the present invention, that  
 25 is, component (A), have viscosities of 40 to 2000 SUS (Saybolt Universal Seconds) at 100° F. Preferably they have viscosities of 75 to 500 SUS at 100° F, and most preferably of 100 to 300 SUS at 100° F. These base oils  
 30 may be natural oils, synthetic oils, or they can be combinations of two or more of these types of oils; e.g. combinations of different natural oils, combinations of different synthetic oils, or combinations of one or more natural  
 35 oils with one or more synthetic oils. Selection of materials suitable as base oils is within the skill of the art using the parameters herein set forth. The term "natural oil" is intended to include oils derived from natural sources but  
 40 modified by conventional processes.

When the base oil is a mixture of natural and synthetic oils, the mixture contains 5 to 95 weight percent of at least one synthetic oil. Preferably such mixtures contain 40 to 90%  
 45 natural oil and 60 to 10% synthetic oil. Of course, both the natural oils and synthetic oils can themselves be mixtures of various types of natural oils or synthetic oils.

When the base oils consists of natural oils,  
 50 they are often derived from petroleum, although oils derived from other natural sources such as shale, coal, animals and plants can also be used. Among the general types of petroleum oils useful in the compositions of this invention  
 55 are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by  
 60 those of skill in the art. All that is required of oils useful in this invention is that they have viscosities falling within the above-noted ranges which enable the final composition to  
 65 have the below-recited SAE multigrade pro-

perties and that they be generally compatible with the other components of the gear lubricant and the materials used in construction of the gear assemblies in which they function.

As is noted above, the base oil can consist  
 70 essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and inter-polymers of C<sub>2-12</sub> olefins, carboxylic acid esters of both  
 75 monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are  
 80 homo- and interpolymers of C<sub>2-12</sub> monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)-  
 85 benzenes, wax-alkylated naphthalenes): and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified  
 90 by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g. methyl polyisopropylene glycol ether having an  
 95 average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and poly-  
 100 carboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>n</sub> fatty acid esters, or the C<sub>13</sub> Oxo acid diester of tetraethylene glycol. Among such glycols are the  
 105 polyalkylene glycols sold by the Union Carbide Corporation of New York under the names UCON LB-135, UCON LB-385 and UCON LB-1145 (UCON is a Trade Mark).

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g. 110 phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g. butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene  
 115 glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl)-  
 120 sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Among the halogenated  
 125 hydrocarbons which may be used as base oils are chlorinated phenyl and biphenyls, low molecular weight chlorotrifluoroethylene polymers, and polytetrafluoroethylenes of appropriate molecular weights. 130

Esters which may be used as synthetic oils also include those made from  $C_3$  to  $C_{12}$  monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol and dipentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of synthetic lubricants (e.g. tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, poly(methyl)siloxanes, and poly-(methylphenyl)siloxanes. Among these are the oils sold by the Dow Chemical Co., of Michigan, under the names DC-200, DC-500 and DC-700 (DC is a Trade Mark). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g. tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid).

Organic carbonates and thiocarbonates such as those formed from the well known Oxo alcohols as well as orthoformates, mercaptals, thiol or thioformates and the like can also be used as synthetic oils in this invention, if in the form they are used (e.g. as blends) they exhibit viscosities within the aforesaid limits.

The fact that the base oils of this invention may consist of natural, synthetic, or natural-synthetic blended oils does not mean that these three types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium) which are used in certain specialized gear assemblies. In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the three types of base oils discussed above may be used in the compositions of the present invention, they are not necessarily functional equivalents of each other in every instance.

It is preferable that, particularly if the lubricants of the present invention consists essentially of only one synthetic base oil and only one polymer, i.e. component (C), the base oil should not be derived from the same olefin as the polymer. Thus, for example, if the polymer is a polybutene, it is preferable that the base oil not consist essentially of only polybutene. If, however, the base oil is a polypropylene or a mixture of polybutene and mineral oil, then the polymer can be a polybutene and so forth.

As is clear from the above discussion, in certain embodiments of this invention the synthetic oil is not solely hydrocarbon in nature, but can contain atoms of oxygen, sulfur, silicon, halogen, as well as those of carbon and hydrogen; of course, in other embodiments the synthetic oil will be solely

hydrocarbon in nature. This is also true of the natural oils used in this invention.

In many embodiments it is preferable that the synthetic oil have a number average molecular weight below about 800. Naturally, such oils must also conform to the viscosity limitations set forth above.

A second component of the gear oils of this invention, that is, component (C), is at least one oil-soluble polymer selected from homopolymers of non-aromatic monoolefins having at least three carbon atoms.

The characterization of these polymers as oil-soluble does not necessarily mean they are soluble in all base oils in all proportions; it means they are soluble in the base oils with which they are formulated to a degree sufficient to allow the lubricant composition to be multi-graded between SAE 75W and SAE 250. These polymers have the common property of having number average molecular weights within the range of 750 to 10,000; preferably their molecular weights lie between 900 and 5,000.

The above-mentioned homopolymers can be prepared from non-aromatic monoolefins having at least three carbon atoms and preferably no more than twenty carbon atoms by a number of polymerization techniques well known to those of skill in the art. It should be noted that "homopolymer" as used herein, describes polymers made from monoolefins having the same number of carbon atoms. Thus, polymers made from a mixture of butene-1 and isobutylene are, in the terms of this specification and the appended claims, homopolymers of butylene. When they contain predominantly units derived from a single isomer, they may be referred to as polymers of that isomer; but, such terminology does not exclude the possibility of the presence of a minor amount of units derived from other isomers. Thus, a "polyisobutylene" might contain units, 80% of which are derived from isobutylene, 15% from 1-butene and 5% from 2-butene.

Particularly preferred are homopolymers made from  $C_3$  to  $C_{20}$  monoolefins such as propene, 2-butene, isobutene, hexene-1, decene-3, and tetradecene-4. More preferable are homopolymers derived from  $C_4$  to  $C_8$  1-olefins such as butene, isobutene, pentene-1, and heptene-1. The most preferred homopolymers are those of propene and the various butenes.

Techniques such as Ziegler, cationic, free-radical, anionic, emulsion polymerization and so forth can be used in appropriate circumstances to prepare these polymers. A particularly convenient technique for polymerizing such olefins for use in this invention is through the use of a Lewis acid catalyst such as aluminum chloride, boron trifluoride or titanium tetrafluoride. These polymerizations are well known in the art and need not be described further at this point.

Among the polymers that may be used in the compositions of the present invention are the following: a polyisobutene of  $\overline{M}_n$  1300, a poly(1-octene) of  $\overline{M}_n$  4300, a poly(3-heptene) of  $\overline{M}_n$  900, a poly(1-eicosene) of  $\overline{M}_n$  of 9500, a poly(1-nonene) of  $\overline{M}_n$  3700, a poly(2-methyl-1-pentene) of  $\overline{M}_n$  1700, a poly(5-ethyl-1-hexene) of  $\overline{M}_n$  of 2200, and a poly(8-methyl-1-tetradecene) of  $\overline{M}_n$  1900.

In general, it is preferred that the polymers of the present invention, i.e. component (C), for reasons of oxidative stability, contain no more than five percent unsaturation on the basis of the total number of carbon-to-carbon covalent linkages present within an average molecule. Such unsaturation can be measured by a number of means well known to those of skill in the art, such as infrared or NMR. Most preferably these polymers contain no discernible unsaturation.

A particularly preferred polymer meeting all the above requirements is polyisobutene, although other polymers such as polypropylene may also prove equally useful and desirable.

The third component, i.e. component (B), of the lubricant compositions of this invention, is an oil-soluble extreme pressure agent, or a combination of two or more such agents. Substances which function as extreme pressure agents in lubricating oils are of an extremely diverse nature as is well known to those of skill in the art. See, for example, the particularly useful discussions in the books "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967), pages 9 et seq.; "Gear and Transmission Lubricants", by C. T. Boner (Reinhold Publishing Corp., New York, 1964), pages 85-100; and "Lubricant Additives" by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973), pages 146-221. These publications are expressly incorporated herein by reference for their discussion of how to make and/or use extreme pressure agents as well as for their discussion of the state of the art with regard to extreme pressure agents.

Among the types of compounds known by those skilled in the art to be usable as extreme pressure agents in the lubricating compositions and, therefore, usable as component (B) of this invention, are organo-boron, organo-sulfur, organo-halogen, organo-halosulfur, organo-phosphorus, organo-halophosphorus, and organo-thiophosphorus compounds as well as esters, amides, and salts of phosphorus and carboxylic acids and oil-soluble molybdenum-containing complexes such as those disclosed in U.S. patent 3,541,014. This patent is hereby incorporated by reference for its discussion of such complexes. Each of these types of compounds can be exemplified by the following:

(1) Borate esters of  $C_{1-4}$  alkanols and adducts prepared by reaction of succinimides of polyalkylene amines and boric acid. Specific

examples include trioctyl borate and the adduct formed by reaction of boric acid with a polyisobutenyl-succinimide of tetraethylene pentamine.

(2) Sulfurized olefins, sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins, trithiones, thienyl derivatives, sulfurized terpenes, sulfurized oligomers of  $C_{2-4}$  monoolefins, xanthates of alkanols and other organo-hydroxy compounds such as phenols, thiocarbamates made from alkyl amines and other organo amines; sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent RE 27,331. Specific examples include sulfurized polyisobutene of  $\overline{M}_n$  1100, sulfurized triisobutene, dicyclohexyl disulfide, diphenyl and dibenzyl disulfide.

(3) Chlorinated waxes of both the paraffinic and microcrystalline type, polyhaloaromatics such as di- and trichlorobenzene, trifluoromethyl naphthalenes, perchlorobenzene, pentachlorophenol and dichloro diphenyl trichloroethane.

(4) Chlorosulfurized olefins and olefinic waxes, sulfurized chlorophenyl methyl chlorides and chloroxanthates, specific examples include chlorodibenzyl disulfide, chlorosulfurized polyisobutene of  $\overline{M}_n$  600, chlorosulfurized pinene and lard oil.

(5) Trialkyl and triaryl phosphites, phosphonates and phosphates, and dihydrocarbyl phosphites; such as tricresyl phosphate, tributyl phosphite, tris(2-chloroethyl)phosphate and phosphite, dibutyl trichloromethyl phosphonates, di(n-butyl)phosphite, and tolyl phosphinic acid dipropyl ester.

(6) Metal dithio dihydrocarbyl phosphates, particularly those of lead and zinc, phosphorus pentasulfide-olefin reaction products, esters of dithiophosphorus acids, esters and salts of thio and dithiophosphates. Specific examples include lead, zinc and sodium dioctyl dithiophosphates, and lead and zinc dibenzyl dithiophosphates.

(7) Reaction products of olefin oxides (e.g., ethylene and propylene oxide) and phosphorus halides oxyhalides or thiohalides, reaction products of phosphites and chloral or bromal, chloro- and bromo-alkyl phosphites and phosphates and amine salts thereof.

(8) Phosphate salts of amines, ammonia and metals, analogous phosphonic acid derivatives, neutral phosphites, phosphonites, phosphates and phosphonates and their thioanalogs. Specific examples include the dihexyl ammonium salt of trichloromethane phosphonic acid, and the diethyl hexyl ammonium salt of dioctyl dithiophosphate.

(9) Fatty acids, dimerized and trimerized unsaturated natural acids (e.g., linoleic) and esters, amine, ammonia, and metal (particularly lead) salts thereof, and amides and imidazoline salt and condensation products thereof, oxazolines, and esters of fatty acids, such as ammonium di-(linoleic) acid, lard oil, oleic

acid, animal glycerides, and lead stearate.

Many of these extreme pressure agents and further specific examples are described in detail in the aforementioned books, "Lubricant Additives" and "Gear and Transmission Lubricants".

Particular classes of extreme pressure agents usable in this invention are the sulfurized hydrocarbons and organo-thiophosphonyl salts, and mixtures of such compounds. The preparation of such compounds is well known in the art. See, for example, the disclosures of U.S. Patents 3,231,558 and 3,197,405, and the above-noted books which are hereby incorporated by reference. In brief, the organo-sulfur compounds are made by reacting an organic material such as isobutylene with a halosulfurizing agent such as sulfur monochloride and subsequently treating the intermediate formed with a sulfurizing agent such as sodium sulfide or polysulfide to produce the desired organo-sulfur extreme pressure agent. The organo-thiophosphorus compounds are conveniently made by reacting a phosphorus sulfide (e.g.  $P_4S_{10}$ ) with a mercaptan or alcohol.

At least one of the afore-mentioned extreme pressure agents is present in the compositions of this invention in an amount sufficient to improve the extreme pressure properties of the composition. Normally, the amount of extreme pressure agent will be 0.25 to 20 weight percent of the total composition. More preferably, it is in the range from 0.5 to 10 weight percent of the total composition.

Often it is desirable to use combinations of two or more of the above-described extreme pressure agents. Such combinations can include mixtures of two or more compounds selected from a single class, or compounds selected from two or more classes of extreme pressure agents. Whatever the particular combination

is, however, the total amount of extreme pressure agent will fall within the above-recited ranges.

Lubricating oils for gears can be classified according to a scheme introduced by the American Society of Automotive Engineers (SAE). According to this so-called SAE classification such lubricating oils are classified into two groups on the basis of their minimum viscosities at 210° F., (98° C). These groups are the winter grades and the normal grades. Each of the two groups is divided into a number of classes. The classes of the winter grades are indicated with the letter W preceded by a number, e.g., a 75W, 80W or 85W oil. The classes of the normal grades are indicated by a number only, viz. a 90, 140 or 250 oil. Generally, oils complying to a certain winter grade do not comply with the viscosity requirement for any normal grade as well, and, conversely, oils complying to a certain normal grade do not comply with the viscosity requirement for a winter grade. Lubricating oils that fall within one SAE class only (viz. either comply with a normal or a winter grade) are designated as single-grade lubricating oils. Examples of widely used single-grade lubricating oils are SAE 75W and SAE 90 oils. On the other hand, lubricating oils which do in fact comply with the specification of both a winter grade and a normal grade are designated multi-grade lubricating oils.

It is a particular feature of the compositions of this invention that they may be multi-graded according to SAE standards within the multigrade range lying between SAE 75W and SAE 250. This means that the compositions have viscosities which allow them to be characterized as multigrade. The viscosity properties required to be exhibited by compositions meeting such standards are summarized in the following table:

TABLE I

|                        | SAE<br>75W | SAE<br>80W | SAE<br>85W | SAE<br>90 | SAE<br>140 | SAE<br>250 |
|------------------------|------------|------------|------------|-----------|------------|------------|
| Vis. @ 210°F(99°C) (a) |            |            |            |           |            |            |
| Min. (cS) (b)          | 4.2        | 7.0        | 11.0       | 14.0      | 25.0       | 43.0       |
| Max. (cS)              | no req.    | no req.    | no req.    | 25.0      | 43.0       | no req.    |
| Min. (SUS) (c)         | 40.0       | 49.0       | 63.0       | 74.0      | 120.0      | 200.0      |
| Max. (SUS)             | no req.    | no req.    | no req.    | 120.0     | 200.0      | no req.    |

(a) Viscosities determined by ASTM D-445 procedure as set forth by the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103, U.S.A.

(b) Centistokes

(c) Saybolt Universal Seconds

In addition, the maximum temperatures for a viscosity of 150,000 cP in the winter grade oils are 75W: -40° F; 80W: -15° F; and 85W: +10° F.

Thus the lower SAE value is the minimum viscosity the oil can have (and still meet the standard), while the upper value is the maximum viscosity the oil can have. For example, an oil multigraded as SAE 75W/90 conforms to the SAE 75W requirement at low temperatures and has a viscosity in the range provided for SAE 90 at 210° F.

It is these viscosity properties which make the compositions of this invention useful since they can function satisfactorily over a wide range of temperatures. Thus, the compositions can function to lubricate a gear at extremely cold temperatures during start-up or while flying at high altitude and still maintain satisfactory lubricating properties well after operation of the gear has resulted in a substantial increase in temperature or the gear-containing device has returned to a warm environment.

Many of the preferred embodiments of this invention are also characterized by properties which permit them to conform with the requirements of MIL-L-2105B specifications promulgated by the U.S. Government for gear lubricants. They thus possess adequate properties with respect to foaming, thermal and oxidative stability, water separation, compatibility and copper corrosion.

In addition to the three essential components discussed above, the compositions of this invention can also include other conventional lubricant additives which confer a variety of beneficial properties upon the composition. Such additives as antioxidants such as hindered alkyl phenols (e.g., 2,6-Di-t-butyl-4-methyl phenol); rust inhibitors such as alkylated succinic acids and anhydrides or calcium, barium or sodium sulfonates; ashless detergent/dispersants such as those noted below; ash-forming detergent/dispersants such as metal phenates and sulfonates; anti-foaming agents, such as silicones, anti-friction agents, such as stearyl alcohol or stearyl cyanide; dyes, metal deactivators and so forth may be included in appropriate amounts, in the composition of this invention.

Among the ashless detergent/dispersants which can be used to advantage in the oil compositions of this invention are those which are formed by reaction of a monoalcohol or polyol with a high molecular weight mono- or polycarboxylic acid acylating agent containing at least thirty carbon atoms in the acyl moiety. Such ester compositions are well known to those of skill in the art. See, for example, French Patent Specification 1,396,645, British Patent Specifications 981,850; 1,055,337; and 1,306,529 as well as U.S. Patents 3,255,108; 3,311,588; 3,311,776; 3,346,345; 3,381,022; 3,522,179; 3,542,680; 3,576,743; 3,579,450; 3,632,510; and 3,659,242. Each of the fore-

going British and foreign patent publications is expressly incorporated herein by reference for their descriptions of how to make and use such compositions.

Another type of particularly useful ashless dispersant is formed by the reaction of a mono- or polycarboxylic acid acylating agent with polyamines. Other related useful dispersants can be prepared by post-treating such dispersants with alkoxides, cyanides, etc. See, for example, U.S. Patents, RE 26,433; 3,172,892; 3,216,936; 3,219,666; 3,256,185; 3,272,746; 3,278,550; 3,306,493; 3,341,542; 3,366,569; 3,373,111; 3,374,174; 3,502,677; 3,541,012. Other useful ashless dispersants are formed by the reaction of a halogenated polymer with a polyalkylene polyamine. Such dispersants are described in U.S. Patents 3,573,010; 3,574,576; 3,438,757; 3,565,804; and 3,565,492. Still other ashless dispersants are formed by reaction of an alkylated phenol, a lower aldehyde and an amine or polyamine via the well-known Mannich reaction. Such materials are disclosed in U.S. Patents 3,036,003; 3,368,972; 3,413,347; 3,448,047; 3,539,633; and 3,649,229. The above U.S. Patents are expressly incorporated herein by reference for their discussion of the preparation and use of such materials in lubricants.

A particularly useful type of additive often included in compositions of this invention is one or more pour point depressants. The use of such pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the aforementioned book "Lubricant Additives" by Smalheer and Smith, page 8, and "Gear and Transmission Lubricants", p. 102, and "Lubricant Additives" by Ranney. Among the types of compounds which function satisfactorily as pour point depressants in the composition of the present invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. A particularly useful class of pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. patent 3,250,715 which is hereby incorporated by reference by reference for its relevant disclosures. Generally, when they are present, in the compositions of this invention, the pour point depressants are present in the amount of 0.01 to 5 weight percent of the total composition.

#### EXAMPLES.

A number of compositions embodying the present invention are prepared by blending together the components outlined in Table II in the indicated proportions which are all percentages by weight. The viscosity properties

- of these compositions are also summarized in Table II. It should be noted that where the percentages of components does not add up to 100, the balance of the composition consists of a pour point depressing terpolymer of a  $C_{12}$ — $C_{14}$  fumarate diester, ethyl vinyl ether and vinyl acetate.
- 5 The extreme pressure agents used in preparing these blends of Examples 1—10 are all commercially available mixtures comprising organo-thiophosphonyl salts and sulfurized hydrocarbons sold by The Lubrizol Corporation of Cleveland, Ohio, under the names *Anglamol* 93, *Anglamol* 98A, and *Anglamol* 99 (*Anglamol* is a Trade Mark).
- 10 As can be seen from an examination of the data in Table II, each of the blends of Examples 1—10 is multigraded according to SAE standards between SAE 75W and SAE 250. These blends also satisfactorily lubricate automotive differential gears and exhibit outstanding shear resistant properties over prolonged use.
- 15 Lubricating oil concentrates can also be used conveniently to prepare such compositions. For example, a composition similar to that of Example 6 can be prepared by first forming a concentrate of polymer, extreme pressure agent and pour point depressant in the relative amounts of 62 parts, 16 parts and 1 part in 21 parts of solvent neutral diluent oil (all parts by weight). Such a concentrate is then blended with an equal part of an appropriate synthetic alkylated aromatic oil to form a composition closely resembling that of Example 6.
- 20 The concentrates comprise (A) a diluent oil, (B) at least one extreme pressure agent and (C) at least one oil-soluble homopolymer of a non-aromatic mono-olefin (as defined above), the amounts of (B) and (C) incorporated in said concentrate being such that when 75 to 25 parts by weight of the concentrate is blended with 25 to 75 parts by weight of at least one base oil having a viscosity of 40 to 2000 SUS at 100° F., the resulting blend is a lubricating oil composition multigraded according to SAE standards within the multigrade range of SAE 75W to SAE 250, exhibiting extreme pressure properties.
- 25 For example, these concentrates comprise about 15 to 70 percent of an oil (which can be natural, synthetic or a mixture of the two), 85 to 30 percent of the afore-described polymer and 5 to 30 percent of the afore-described extreme pressure agents. Optionally such concentrates can also contain 0.5 to 5 percent of a pour point depressant.

TABLE II

| Ex. | Base Oil <sup>1</sup>  |                        | Polymer           |      | Extreme Pressure Agent |              | Viscosity Grade |                        |
|-----|--|------------------------|-------------------|------|------------------------|--------------|-----------------|------------------------|
|     | Type   | Amount, % <sup>1</sup> | Type <sup>2</sup> | Mn   | Amount, % <sup>1</sup> | Type         |                 | Amount, % <sup>1</sup> |
| 1   | 350 Solvent Neutral<br>650 Solvent Neutral                         | 46.2<br>30.8           | PBI               | 1300 | 16                     | Anglamol 99  | 7.0             | 80W/90                 |
| 2   | 150 Bright Stock<br>100 Naphthalene Neutral                        | 34<br>34.5             | PBI               | 1300 | 25                     | Anglamol 99  | 6.5             | 80W/140                |
| 3   | 200 Solvent Neutral  | 41.5                   | PBI               | 900  | 50                     | Anglamol 99  | 6.5             | 85W/250                |
| 4   | 200 Solvent Neutral  | 59.5                   | PBI               | 900  | 32                     | Anglamol 98A | 8.0             | 80W/90                 |
| 5   | 200 Solvent Neutral  | 50.5                   | PBI               | 900  | 40                     | Anglamol 99  | 8.5             | 85W/140                |
| 6   | Synthetic Alkylated<br>Aromatics (Mn = 350)<br>100 Solvent Neutral | 50<br>10.5             | PBI               | 900  | 31                     | Anglamol 98A | 8.0             | 75W/90                 |
| 7   | 100 Solvent Neutral<br>Synthetic Alkylated<br>Aromatics (Mn = 350) | 32.25<br>32.25         | PBI               | 1300 | 27                     | Anglamol 99  | 6.5             | 75W/90                 |
| 8   | Pentaerythritol Ester <sup>1</sup>                                 | 59.5                   | PBI               | 900  | 32                     | Anglamol 98A | 8.0             | 80W/90                 |
| 9   | 150 Solvent Neutral  | 45                     | PBI               | 1300 | 45                     | Anglamol 93  | 10.0            | 85W/90                 |
| 10  | 100 Naphthenic Neutral<br>300 Solvent Neutral                      | 45<br>10               | PP                | 1500 | 37                     | Anglamol 98A | 8.0             | 80W/140                |

<sup>1</sup>All amounts in weight percentages<sup>2</sup>PBI = polyisobutylene; PP = polypropylene



## WHAT WE CLAIM IS:—

1. A lubricating oil composition comprising (A) at least 30 weight percent of a base oil having a viscosity of 40 to 2000 SUS at 100° F, (B) at least one extreme pressure agent in an amount sufficient to improve its extreme pressure properties, and (C) at least 5 weight percent of at least one oil-soluble homopolymer (as hereinbefore defined) of a non-aromatic mono-olefin having at least 3 carbon atoms, said polymer having a number average molecular weight of 750 to 10,000 and being present in an amount such as to allow the lubricating oil composition to be multigraded gear oil having a minimum winter grade of SAE 75W and a maximum normal grade of SAE 250; with the proviso that when the base oil is a mixture of synthetic and natural oils (as hereinbefore defined), it contains 5 to 95 weight percent of at least one synthetic oil.
2. A composition as claimed in claim 1 wherein the base oil has a viscosity of 75 to 500 SUS at 100° F.
3. A composition as claimed in claim 2 wherein the base oil has a viscosity of 100 to 300 SUS at 100° F.
4. A composition as claimed in any preceding claim wherein the amount of extreme pressure agent is from 0.25 to 20 weight percent of the total composition.
5. A composition as claimed in any preceding claim wherein the extreme pressure agent is selected from organo-boron-, organo-sulfur, organo-halogen-, organo-halosulfur-, organo-phosphorus-, and organo-thiophosphorus-compounds and esters, amides and salts of phosphorus and carboxylic acids.
6. A composition as claimed in claim 5 wherein the extreme pressure agent is a mixture of organo-thiophosphonyl salts and sulfurized hydrocarbons.
7. A composition as claimed in any preceding claim which also comprises 0.01 to 5 weight percent of at least one pour point depressant.
8. A composition as claimed in claim 7 wherein the pour point depressant is selected from polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds and vinyl carboxylate polymers.
9. A composition as claimed in claim 7 wherein the pour point depressant is a terpolymer of a dialkyl fumarate, an alkyl vinyl

ether, and a vinyl ester of a fatty acid.

10. A composition as claimed in any preceding claim wherein the homopolymer is derived from a  $C_3-C_{20}$  olefin.

11. A composition as claimed in claim 10 wherein the homopolymer is derived from a  $C_4-C_{10}$  1-olefin.

12. A composition as claimed in claim 10 wherein the homopolymer is derived from propene or a butene.

13. A composition as claimed in any preceding claim wherein the polymer has a number average molecular weight of 900—5000.

14. A composition as claimed in claim 1, wherein (A) is present in the amount of 90 to 50 weight percent and has a viscosity of 75 to 500 SUS at 100° F and (B) is present in an amount of 0.25 to 20%, and is selected from organo-thiophosphonyl salts, sulfurized hydrocarbons and mixtures thereof and (C) is present in the amount of 10 to 50 weight percent and its monomer has from 3 to 20 carbon atoms.

15. A composition as claimed in claim 14, wherein the homopolymer is a polyisobutene having a number average molecular weight of 900 to 5,000.

16. A composition as claimed in any preceding claim, wherein the base oil consists essentially of a natural oil.

17. A composition as claimed in any of claims 1—15, wherein the base oil is a mixture of 5 to 95 weight percent natural oil, and 95 to 5 weight percent of at least one synthetic oil and wherein the synthetic oil is not derived from the same olefins as polymer (C).

18. A composition as claimed in any of claims 1—15, wherein the base oil consists essentially of a synthetic oil and wherein the synthetic oil is not derived from the same olefins as polymer (C).

19. A composition as claimed in claim 17 or 18, wherein the synthetic oil is not solely hydrocarbon in composition.

20. A lubricating oil composition as claimed in claim 1 substantially as hereinbefore described in any of the Examples.

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